

# Charge and Orbital Ordering and Spin State Transition Driven by Structural Distortion in $\text{YBaCo}_2\text{O}_5$

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We have investigated electronic structures of antiferromagnetic  $\text{YBaCo}_2\text{O}_5$  using the local spin-density approximation (LSDA) +  $U$  method. The charge and orbital ordered insulating ground state is correctly obtained with the strong on-site Coulomb interaction.  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  ions are found to be in the high spin (HS) and intermediate spin (IS) state, respectively. It is considered that the tetragonal to orthorhombic structural transition is responsible for the ordering phenomena and the spin states of Co ions. The large contribution of the orbital moment to the total magnetic moment indicates that the spin-orbit coupling is also important in  $\text{YBaCo}_2\text{O}_5$ .

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Recently, an interesting spin state transition of the  $\text{Co}^{2+}$  ion in  $\text{YBaCo}_2\text{O}_5$  has been reported by Vogt *et al.* [1] using the neutron powder diffraction (NPD) measurements. The transition is induced by the long-range orbital and charge ordering of  $\text{Co}^{2+}/\text{Co}^{3+}$  ions. The ordered oxygen-deficient double perovskite  $R\text{BaCo}_2\text{O}_{5+\delta}$  ( $R$  = rare-earths) [2] has attracted much attention as a new spin-charge-orbital coupled system like manganites and also as a new Co-based colossal magnetoresistance (CMR) material. Indeed, giant magnetoresistance are observed for  $R=\text{Gd}$  and  $\text{Eu}$ ,  $(\rho_0 - \rho_{H=7\text{T}})/\rho_0 = 41\%$  and  $40\%$  for  $\text{GdBaCo}_2\text{O}_{5.4}$  and  $\text{EuBaCo}_2\text{O}_{5.4}$ , respectively [3].

In the paramagnetic phase,  $\text{YBaCo}_2\text{O}_5$  is crystallized in the tetragonal structure of the space group  $P4/mmm$ . It consists of double  $\text{CoO}_5$  square base pyramidal backbone layers along the  $c$ -axis in which Y and Ba layers intervene alternatively and oxygens are deficient exclusively from the Y layers [2–4]. According to the valency consideration,  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  ions coexist similarly as the  $\text{Mn}^{3+}/\text{Mn}^{4+}$  covalency in hole-doped  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ . Below  $T_N \sim 330$  K,  $\text{YBaCo}_2\text{O}_5$  undergoes a *G*-type antiferromagnetic (AFM) transition and the lattice changes slightly from the tetragonal to orthorhombic structure [1]. At  $T_{\text{CO}} \sim 220$  K, a pronounced upturn is observed in the resistivity indicating that another transition takes place, *i.e.*, the long-range charge and orbital ordering of  $\text{Co}^{2+}/\text{Co}^{3+}$  ions. The stripe type charge ordering is formed in the  $ab$  plane. Further, the spin state of the  $\text{Co}^{2+}$  ion changes from the low to high spin across  $T_{\text{CO}}$ , which is evidenced by the increased magnetic moment per Co ion from  $2.10\mu_B$  at 300 K to  $3.45\mu_B$  at 25 K. More recently, for the isostructural  $\text{HoBaCo}_2\text{O}_5$ , essentially the same features are observed of  $T_N \sim 340$  K and  $T_{\text{CO}} \sim 210$  K [5].

The phenomenon of the spin state transition is observed usually in cobaltates such as  $\text{LaCoO}_3$  and  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ . In  $\text{LaCoO}_3$ , the magnetic ground state of  $\text{Co}^{3+}$  ion corresponds to the low spin (LS) state with  $t_{2g}^6e_g^0$ . Upon heating, a successive spin state transition to an intermediate spin (IS) state and then to a high spin (HS) state occurs [6]. Note that, distinctly from the case

in  $\text{LaCoO}_3$ , the spin state transition in  $\text{YBaCo}_2\text{O}_5$  seems to occur for  $\text{Co}^{2+}$  ion. In fact, this issue is still controversial. Based on the reduction of the magnetic susceptibility below 220K, Akahoshi and Ueda [7] suggested that the AFM transition takes place at  $T \sim 220$  K which is associated with a spin state transition of  $\text{Co}^{3+}$  from the HS to LS state upon cooling. Thus, the nature of the spin state transition and the interplay of the spin state with the charge and orbital ordering are still unclear.

To reveal the mechanism of the spin state transition as well as the charge and orbital ordering, we have explored the electronic structure of the *G*-type AFM  $\text{YBaCo}_2\text{O}_5$  using the local-spin density approximation (LSDA) +  $U$  scheme implemented in the linearized muffin-tin orbital band method [8,9].

We have employed two structural data of nearly tetragonal structure at 300 K (L1) and orthorhombic structure at 25 K (L2) [1]. In the L1 structure, all the Co sites have an equal average bond length of  $d(\text{Co-O}) = 1.97$  Å. Whereas in the L2 structure, there are two different kinds of Co sites, CoI and CoII. The bond length at CoI sites is extended to  $d(\text{CoI-O}) = 2.03$  Å and that at CoII sites becomes shortened to  $d(\text{CoII-O}) = 1.92$  Å. The *G*-type AFM spin order is assumed in all our calculations.

In Fig. 1, we have compared the LSDA Co 3d partial density of states (PDOS) for the L1 and L2 structures. Most notable is the change of the exchange splitting which becomes larger for CoI site and smaller for CoII in L2 than that for Co in L1. This indicates that, due to the lattice distortion, 3d electrons in L2 becomes more localized for CoI and less localized for CoII in comparison to those for Co in L1. The calculated spin magnetic moments are  $\mu_S = 1.68\mu_B$  and  $0.95\mu_B$  for each CoI and CoII site, respectively, in L2 and  $\mu_S = 1.13\mu_B$  for Co in L1. The sizes of the spin moments are consistent with the degree of 3d electron localization. Hence, the LSDA gives a qualitatively good information about the structural transition effects on Co 3d electron states. The LSDA, however, yields an incorrect metallic ground state which pertains even after the structural transition from the L1 to L2 structure. This is different from the experiment which shows unambiguously the semiconducting

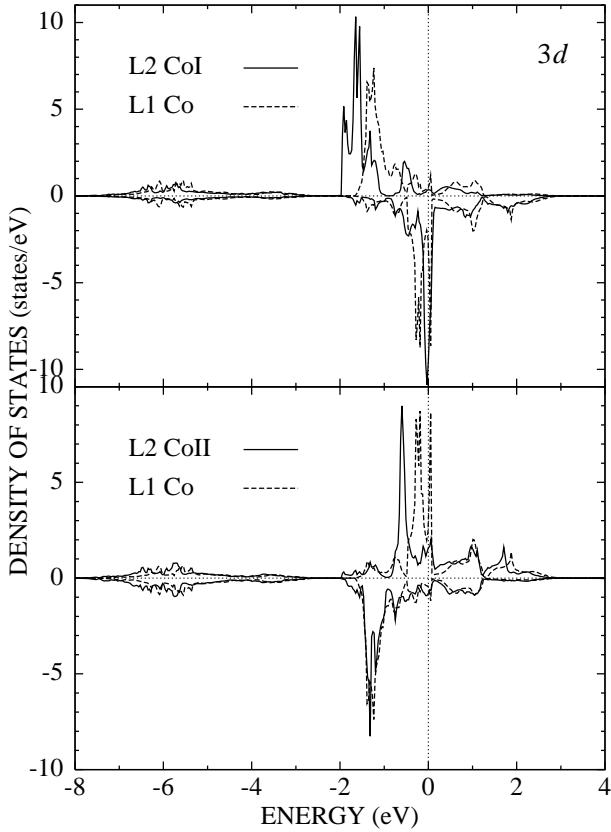


FIG. 1. The LSDA PDOS of Co 3d electrons in the L1 (300 K phase) and L2 (25 K phase) structures. In L2, there are two different types of Co sites, CoI and CoII. Neighboring CoI and CoII sites are polarized antiferromagnetically. As manifested by the exchange splitting, 3d electrons are more localized for CoI site and less localized for CoII than those for Co in L1.

resistivity behavior below 220 K [1,5,7].

Using the LSDA, one cannot expect proper description of localized Co 3d electrons in  $\text{YBaCo}_2\text{O}_5$ . To resolve the above problem, we have applied the LSDA +  $U$  method with parameter values of  $U = 5.0$  eV and  $J = 0.89$  eV. Although there is an arbitrariness of the  $U$ -value in our calculation, the LSDA +  $U$  results are usually not much sensitive to the used  $U$ -value within  $\Delta U \sim \pm 1$  eV [10]. The spin-orbit interaction is also taken into account in the self-consistent variational loop, because Co 3d electrons are expected to retain atomic properties to some extent due to their localized nature.

Figures 2 and 3 present CoI and CoII 3d PDOS, respectively, in the L2 structure obtained by the LSDA +  $U$  calculations. In the bottom panels,  $t_{2g}$  and  $e_g$  decompositions of 3d PDOS are also provided. It is amusing to note that the energy gap of  $E_g \sim 0.6$  eV opens at the Fermi level  $E_F$  and so  $\text{YBaCo}_2\text{O}_5$  becomes an insulator as expected in consideration of the  $\text{Co}^{2+}/\text{Co}^{3+}$  charge ordering. For CoI 3d electrons, the majority-spin bands are fully occupied by three electrons in  $t_{2g}$  and two electrons in  $e_g$  bands. The minority-spin  $t_{2g}$  bands are only

partially occupied by two electrons, and one  $t_{2g}$  and two  $e_g$  bands are almost empty. Considering the pyramidal environment of Co, the occupied  $t_{2g}$  states corresponds to  $d_{zx}$  and  $d_{yz}$  while the empty  $t_{2g}$  to  $d_{xy}$ . Accordingly, the nominal valency and the 3d electron configuration at CoI site are assigned to be  $\text{Co}^{2+}$  and  $3d^7$  ( $t_{2g}^5 e_g^2$ ), respectively [11]. Hence,  $\text{Co}^{2+}$  ion is in the HS state with spin magnetic moment of  $\mu_S = 3\mu_B$  ( $S = 3/2$ ), which is consistent with the NPD data.

For CoII 3d electrons, the majority-spin bands are not fully occupied with a split-off empty  $e_g$  state above  $E_F$  (see Fig. 3). For the minority-spin bands, the situation is similar to the case of CoI. It is thus possible to identify the 3d electron configuration of CoII as  $3d^6$  ( $t_{2g}^5 e_g^1$ ) and the valency as  $\text{Co}^{3+}$ . With one less electron than  $\text{Co}^{2+}$ , the lower  $d_{3z^2-r^2}$  out of two  $e_g$  states in the majority-spin bands is occupied and the upper  $d_{x^2-y^2}$  becomes empty. Hence, the spin state of  $\text{Co}^{3+}$  ion is the IS state which is also in agreement with the experimental analysis of  $\mu_S = 2\mu_B$  ( $S = 1$ ).

The calculated charge occupancies of each Co 3d orbitals are shown in Table I. For  $\text{Co}^{2+}$  ion, the majority-spin bands are almost completely occupied by  $t_{2g} \uparrow = 2.98$  and  $e_g \uparrow = 1.99$  electrons, while the minority-bands are only partially occupied by  $t_{2g} \downarrow = 2.02$  and  $e_g \downarrow = 0.37$  electrons. For  $\text{Co}^{3+}$  ion, it is noticeable that the majority-spin  $e_g$  states are partially occupied by  $e_g \downarrow = 1.54$  electrons. Hence, the calculated charge occupancies are consistent with the nominal valencies of  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$ , if one takes into account the band hybridization effects.

Vogt *et al.* [1] have deduced magnetic moments from the NPD experiments as  $\mu_{\text{exp}} = 4.2\mu_B$  and  $2.7\mu_B$  for each  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  ion, respectively. In the analysis of the experiments, they counted only the spin moment contribution, assuming that the orbital moment is quenched. However, the orbital moment is only partially quenched in  $\text{YBaCo}_2\text{O}_5$ . In Table I, we have summarized the calculated magnetic moments using the LSDA +  $U$

TABLE I. The calculated charge occupancies of Co 3d orbitals (electrons) and magnetic moments ( $\mu_B$ ) of  $\text{YBaCo}_2\text{O}_5$  in the LSDA +  $U$  method.

	$\text{Co}^{2+}$	$\text{Co}^{3+}$
$t_{2g} \uparrow$	2.98	2.14
$e_g \uparrow$	1.99	0.60
$t_{2g} \downarrow$	2.02	2.99
$e_g \downarrow$	0.37	1.54
$\mu_S$	2.61	1.84
$\mu_L$	1.04	0.40
$\mu_{\text{tot}}$	3.65	2.24
$\mu_{\text{exp}}$	$4.2^a, 3.7^b$	$2.7^{a,b}$

<sup>a</sup> Reference [1].

<sup>b</sup>  $\text{HoBaCo}_2\text{O}_5$  in Ref. [5]. The assignment of the magnetic moments to each Co ion is corrected (see text).

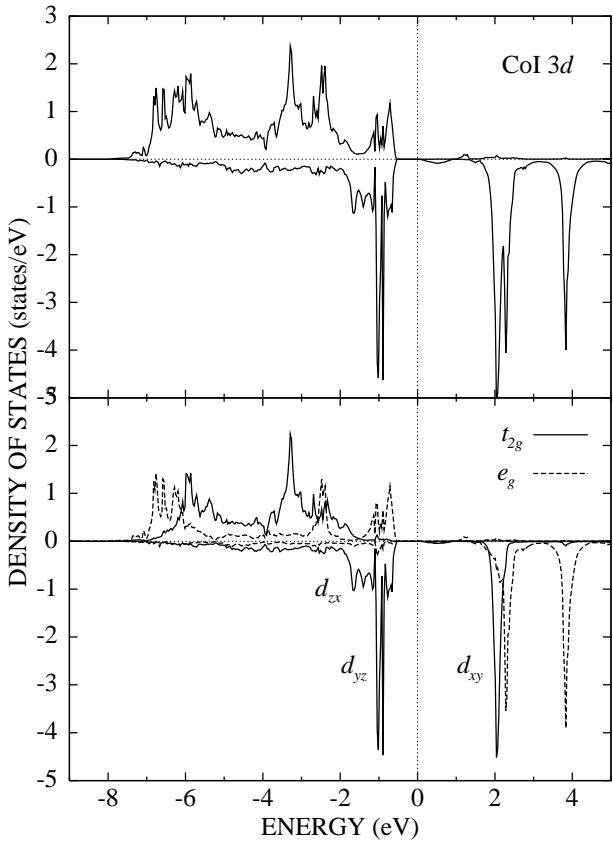


FIG. 2. The LSDA +  $U$  PDOS of CoI 3d electrons in the L2 (25 K phase) structure. In the bottom panel,  $t_{2g}$  and  $e_g$  decompositions of 3d PDOS are also provided. The majority-spin bands are fully occupied, while in the minority-spin bands, only 2/3 states of  $t_{2g}$  bands are occupied. The nominal valency of CoI site is  $\text{Co}^{2+}$  with  $3d^7$  ( $t_{2g}^5 e_g^2$ ).  $\text{Co}^{2+}$  ion is in the HS state.

method. For  $\text{Co}^{2+}$  ion, the spin and orbital magnetic moments are  $\mu_S = 2.61\mu_B$  and  $\mu_L = 1.04\mu_B$ , respectively, and for  $\text{Co}^{3+}$  ion,  $\mu_S = 1.84\mu_B$  and  $\mu_L = 0.40\mu_B$ . The orbital moment of  $\text{Co}^{2+}$  ion is as much as that of CoO [12,13], and the orbital moment of  $\text{Co}^{3+}$  is comparable to that of NiO [10,14]. The non-negligible orbital moment, which originates from the localized nature of Co 3d electrons, suggests that  $\text{YBaCo}_2\text{O}_5$  should fall in a class of strongly correlated electron system like CoO and NiO. The calculated total magnetic moments of  $\mu_{\text{tot}} = 3.65\mu_B$  and  $2.24\mu_B$  for  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  ion, respectively, are only slightly smaller than the experimental values. Evidently, this interpretation will also be valid for  $\text{HoBaCo}_2\text{O}_5$ . Suard *et al.* [5] have improperly assigned the NPD measured  $\mu_{\text{exp}} = 3.7\mu_B$  and  $2.7\mu_B$  in  $\text{HoBaCo}_2\text{O}_5$  to  $\text{Co}^{3+}$  and  $\text{Co}^{2+}$  ion, respectively. However, their assumptions of spin-only moments and the HS states for both  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  ions are discarded by the present results. To test the calculated results, more experimental works like the x-ray scattering measurement are encouraged, in which separate determination of the spin and orbital moments are possible.

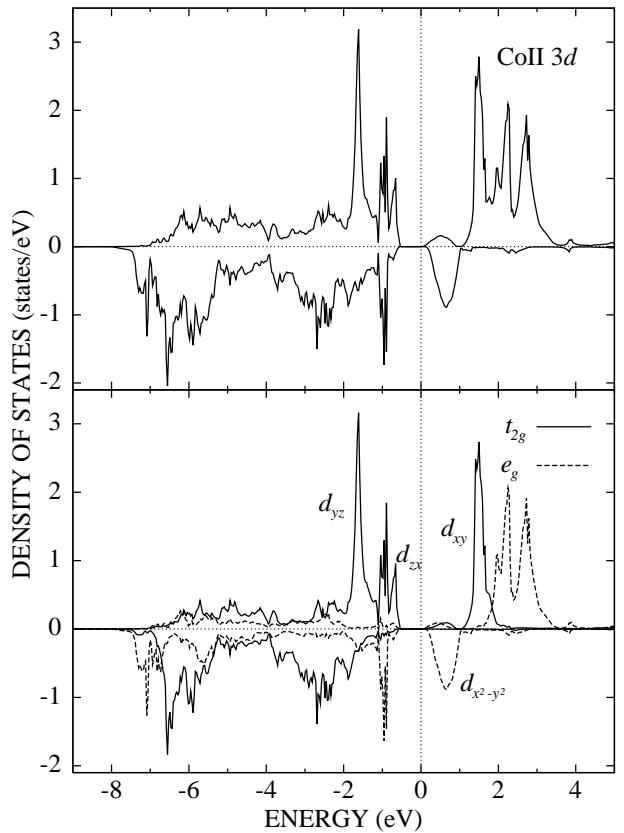


FIG. 3. The LSDA +  $U$  PDOS of CoII 3d electrons in the L2 (25 K phase) structure which is antiferromagnetically polarized to that of neighboring CoI. Unoccupied  $e_g$  states in the majority-spin bands are clearly visible above  $E_F$ . The valency and the 3d electron configuration of CoII site is nominally identified as  $\text{Co}^{3+}$  and  $3d^6$  ( $t_{2g}^5 e_g^1$ ), respectively.  $\text{Co}^{3+}$  ion is in the IS state.

In Fig. 4, we have plotted the geometry of the orbital ordering which is obtained from the orbital dependent occupancy of the 3d minority-spin states at each Co site. At  $\text{Co}^{2+}$  sites, the orbitals are aligned along  $a$ -axis, while at  $\text{Co}^{3+}$  sites, the orbitals are along  $b$ -axis. This feature is understandable by considering that the bond length of  $d(\text{Co}^{2+}\text{-O})$  is larger in  $a$ -axis than in  $b$ -axis and *vice versa* for that of  $d(\text{Co}^{3+}\text{-O})$ . As for the charge ordering configuration,  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  chains of a stripe type are formed in the  $ab$  plane along  $b$ -axis, which are alternating in the  $a$  and  $c$  direction [1,5]. This is in contrast to the charge ordering observed in the isostructural  $\text{YBaMn}_2\text{O}_5$ . In  $\text{YBaMn}_2\text{O}_5$ , the  $\text{Mn}^{2+}/\text{Mn}^{3+}$  orders in a checkerboard type [15]. This difference gives rise to the different magnetic structures: *G*-type AFM phase for  $\text{YBaCo}_2\text{O}_5$  and *G*-type ferrimagnetic phase for  $\text{YBaMn}_2\text{O}_5$ . The theoretical result of the charge and orbital ordering geometry coincides with the experimentally proposed one [1,5]. Thus, it can be inferred that the deformed bond lengths of  $d(\text{Co-O})$  determine the charge and orbital ordering geometry.

The *G*-type AFM ordering in  $\text{YBaCo}_2\text{O}_5$  is consistent

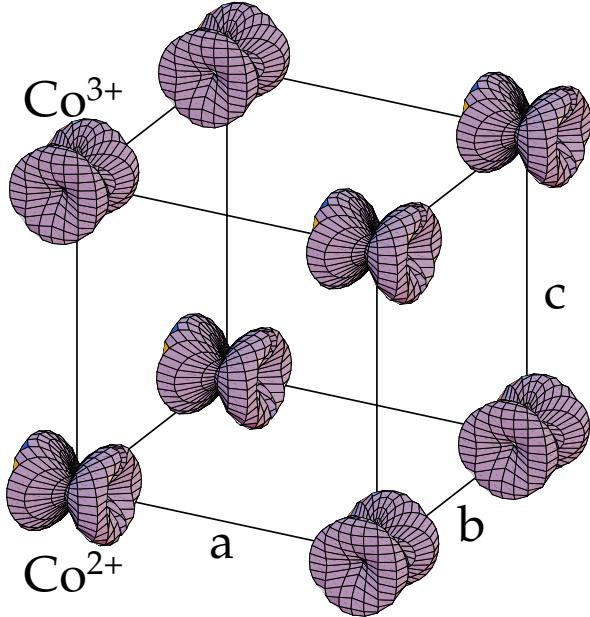


FIG. 4. The orbital ordering geometry of the occupied minority-spin states at each Co site. At  $\text{Co}^{2+}$  sites,  $3d$  orbitals are aligned along the  $a$ -axis while at  $\text{Co}^{3+}$  sites, along the  $b$ -axis.

with the above charge and orbital ordering geometry. In the  $\text{Co}^{3+}$  chains, the kinetic-exchange energy gain between the occupied  $d_{yz}$  and  $d_{zx}$  states and the empty  $d_{x^2-y^2}$  state for the AFM configuration of neighboring sites stabilizes the AFM spin ordering. In a similar way, the AFM ordering between neighboring  $\text{Co}^{3+}$  and  $\text{Co}^{2+}$  ions can be explained. The AFM ordering in the  $\text{Co}^{2+}$  chains, however, is hard to understand in terms of the direct kinetic-exchange gain, because the overlap integral between two neighboring  $\text{Co}^{2+}$  ions would be negligible as seen in Fig. 4. Instead, the AFM interaction in the  $\text{Co}^{2+}$  chains is expected to be derived indirectly via the  $\text{Co}^{2+}$ - $\text{Co}^{3+}$  and  $\text{Co}^{3+}$ - $\text{Co}^{3+}$  AFM interactions.

As mentioned above, the structural transition plays a crucial role in determining the ground state properties of  $\text{YBaCo}_2\text{O}_5$ . Although the tetragonal to orthorhombic structural transition occurs simultaneously with the  $G$ -type AFM transition at  $T_N \sim 330$  K, the structural deformation is not significant above 220 K. Only near  $T_{\text{CO}} \sim 220$  K, the lattice splitting between  $a$ - and  $b$ -axis becomes pronounced and the charge and orbital ordering emerges with the  $\text{Co}^{2+}$  spin state transition from the low to high spin. Furthermore, it is known that the long-range charge ordering and the spin state transition are very sensitive to the oxygen stoichiometry [1]. Therefore, the structural distortion is thought to be responsible for the orderings and the spin state transition by inducing different local environment at each Co ion site. This feature implies that the electron-lattice interaction is very important in this system. A detailed study on

the electron-phonon interaction effects in  $\text{YBaCo}_2\text{O}_5$  is urgently demanded.

In conclusion, we have performed the LSDA +  $U$  calculations for a new spin-charge-orbital-lattice coupled system  $\text{YBaCo}_2\text{O}_5$ . It is found that the  $\text{Co}^{2+}/\text{Co}^{3+}$  charge and orbital ordering and the  $\text{Co}^{2+}$  HS state transition are closely correlated with the lattice distortion from the tetragonal to orthorhombic structure. The orbital moment has a substantially large contribution to the total magnetic moment. All of the effects of the Coulomb correlation, the spin-orbit coupling, and the electron-phonon interaction should be properly taken into account to understand physical properties of  $\text{YBaCo}_2\text{O}_5$ .

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